# <Advanced Research Center for Beam Science>Electron Microscopy and Crystal Chemistry

# Advanced Research Center for Beam Science
## – Electron Microscopy and Crystal Chemistry –

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## Scope of Research

We study crystallographic and electronic structures of materials and their transformations through direct imaging of atoms or molecules by high-resolution electron spectromicroscopy, which realizes energy-filtered imaging and electron energy-loss spectroscopy as well as high-resolution imaging. By combining this with scanning probe microscopy, we cover the following subjects: 1) direct structure analysis, electron crystallographic analysis, 2) epitaxial growth of molecules, 3) structure formation in solutions, and 4) fabrication of low-dimensional functional assemblies.

**KEYWORDS**
EELS
STEM
Surface Plasmon
Nanoparticle
Substrate Effect

### Selected Publications


Haruta, M.; Kurata, H., Direct Observation of Crystal Defects in an Organic Molecular Crystals of Copper Hexachlorophthalocyanine by STEM-EELS, *Sci. Rep.*, **2,** [252-1]-[252-4] (2012).

Aso, R.; Kan, D.; Shimakawa, Y.; Kurata, H., Atomic Level Observation of Octahedral Distortions at the Perovskite Oxide Heterointerface, *Sci. Rep.*, **3,** [2214-1]-[2214-6] (2013).

Saito, H.; Namura, K.; Suzuki, M.; Kurata, H., Dispersion Relations for Coupled Surface Plasmon-polariton Modes Excited in Multilayer Structures, *Microscopy*, **63,** 85-93 (2014).

Saito, H.; Kurata, H., Formation of a Hybrid Plasmonic Waveguide Mode Probed by Dispersion Measurement, *J. Appl. Phys.*, **117,** [133107-1]-[133107-7] (2015).

Haruta, M.; Hosaka, Y.; Ichikawa, N.; Saito, T.; Shimakawa, Y.; Kurata, H., Determination of Elemental Ratio in an Atomic Column by Electron Energy-Loss Spectroscopy, *ACS Nano*, **10,** 6680-6684 (2016).

## Studying Substrate Effects on Localized Surface Plasmons in an Individual Silver Nanoparticle Using Electron Energy-Loss Spectroscopy

Localized surface plasmons (LSPs) in metallic nanoparticles (NPs) are accompanied by enhanced electromagnetic fields confined within regions smaller than the optical diffraction limit. LSPs in metallic NPs have found applications in biological sensing, solar light harvesting, photocatalysis, optical waveguides and so on. Since LSPs are sensitive to the environment surrounding the NPs as well as to the NP structure, it is important to investigate LSPs in individual NPs supported on substrates with high spatial resolution. In this study, electron energy-loss spectroscopy (EELS) in conjunction with scanning transmission electron microscopy (STEM) was used to investigate LSPs in a single silver NP on a magnesium oxide (MgO) substrate, employing an incident electron trajectory parallel to the substrate surface.

Figure 1 shows the experimental results obtained by high angle annular dark field (HAADF) and spectrum imaging (SI) methods. The substrate effects are clearly evident in the EEL spectra and in the map, and appear as a slight peak shift in the spectra and as the asymmetrical intensity distribution in the map. To understand the substrate effects, we performed the discrete dipoles approximation (DDA) simulations. Figure 2a presents the EEL spectra calculated for three different electron trajectories. The LSP dipole modes for which the polarization is perpendicular or parallel to the substrate are excited by electrons having trajectories A and B, respectively. Polarization perpendicular to the substrate localizes the charges near the substrate surface, resulting in a stronger interaction between the NP and the substrate compared to parallel polarization. Therefore, the resonance energy of the LSP with polarization perpendicular to the substrate is lower than that of the LSP having parallel polarization. The intensity of the LSP peak associated with trajectory A is strong compared to that for an isolated NP, while that for trajectory C is considerably weaker. This characteristic intensity distribution is also noticeable in the LSP map shown in Figure 2b. When the incident electron is located at the top surface of the NP, the polarization field due to the image charge in the substrate enhances the applied field experienced by the NP compared to that which would be generated only by the incident electron, meaning that many dipoles are excited in the NP and leading to the high LSP peak intensity at the top surface of the NP compared to that of an isolated NP, as shown in Figure 2a. In contrast, when the electron is incident in the vicinity of the interface between the NP and the substrate, the applied field in the NP is weak and its distribution is limited to the region near the interface. This is attributed to the strong cancellation in the NP region resulting from the polarization field of the substrate, because the NP is located in the opposite direction to the image charge with respect to the position of the incident electron. Therefore, the energy-loss probability is low in the vicinity of the interface. In the case of an electron travelling near the side of the NP, the applied field distribution in the NP is similar to that in an isolated NP. Therefore, the substrate effect is weak and limited to the region between the incident electron and the interface, leading to a similar LSP peak intensity (Figure 2a).

The resonance energies of LSPs were dependent on the polarization direction relative to the substrate surface. This result is similar to those obtained previously from optical studies using polarized light. However, the LSP maps obtained by STEM-EELS analysis show an asymmetric intensity distribution with the highest intensity at the top surface of the NP (that is, far from the substrate), a result that is not predicted by optical simulations. We show that modifications of the applied electric field by the substrate cause this asymmetric intensity distribution in the LSP maps.

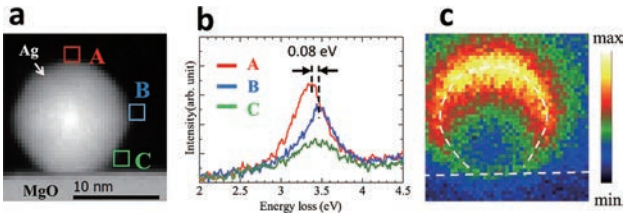


**Figure 1.** Experimental EELS results obtained from a silver NP placed on an MgO substrate, applying electron irradiation in the direction of the cross-section. (a) HAADF image, in which three 2 nm squares are indicated, each 1 nm from the NP surface. (b) EELS spectra obtained from the top, side and gap regions indicated in (a) as A (red), B (blue) and C (green). (c) EELS map generated using an energy window from 3.20 to 3.60 eV.

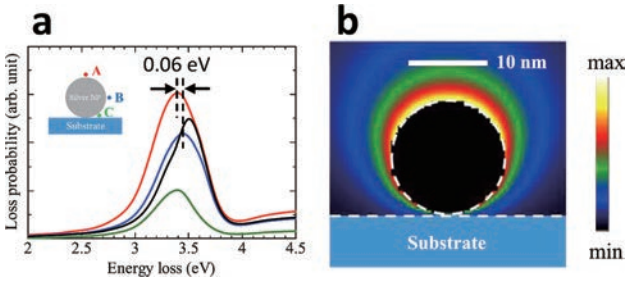


**Figure 2.** The EELS spectra and map calculated for a silver nano-sphere placed on an MgO substrate. (a) EELS spectra calculated for electron trajectories at the top, side and gap regions marked as A (red), B (blue) and C (green) in the inset, and that calculated for an isolated NP in a vacuum (black). These spectra were broadened by the instrumental energy resolution. (b) EELS map calculated at an energy of 3.40 eV.